

PATENT ABSTRACTS OF JAPAN

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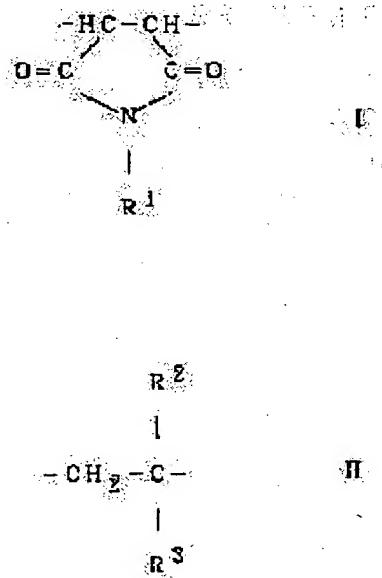
(22)Date of filing : 07.09.1998 (72)Inventor : HARUNARI TAKESHI
DOI TORU

(54) TRANSPARENT FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject film with excellent optical properties, heat resistance, mechanical properties and surface smoothness by using a composition comprising a maleimide-olefin-based copolymer and a copolymer of specific composition.

SOLUTION: This film with a thickness of pref. 10-500 μm is obtained by using a resin composition comprising (A) 1-99 wt.% of a maleimide-olefin copolymer with a number-average molecular weight of 1×10^3 to 5×10^6 composed of 40-60 mol% of constituent of formula I (R_1 is H or a 1-6C alkyl) and 60-40 mol% of constituent of formula II (R_2 and R_3 are each H or a 1-6C alkyl) and (B) 99-1 wt.% of an acrylonitrile-styrene copolymer containing 21-45 wt.% of acrylonitrile unit.



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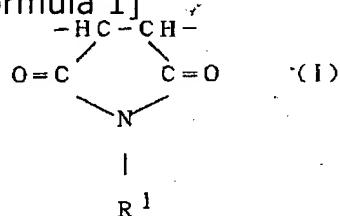
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CLAIMS

[Claim(s)]

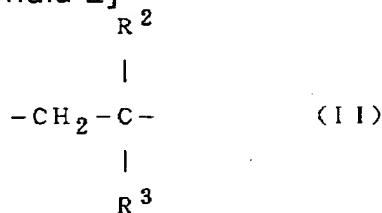
[Claim 1] a) The transparency film with which it is 40 - 60-mol %, a constituent (II) is 60 - 40-mol %, and the constituent (I) shown below is characterized by changing using the resin constituent which consists of 1 - 99 % of the weight of 1x103 or more maleimide olefine copolymers it is [olefine copolymers] 5x106 or less, and 99 - 1 % of the weight of acrylonitrile styrene copolymers which include b acrylonitrile unit 21 to 45% of the weight by number average molecular weight.

[Formula 1]



(R¹は水素または炭素数1～6のアルキル基を示す)

[Formula 2]



(R²及びR³は各々水素または炭素数1～6のアルキル基を示す)

[Claim 2] A transparency film given in the example 1 characterized by the thickness of a transparency film being 10-500 micrometers.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[The technical field to which invention belongs] this invention relates to the transparency film excellent in the optical property and thermal resistance which consist of a maleimide olefin system copolymer and an acrylonitrile styrene copolymer, and the mechanical characteristic.

[0002]

[Description of the Prior Art] The transparency film has been used for various uses by the purposes, such as packing, a surface protection, a display, and the laminating base. And in the electronics field, the alternative to transparent plastic film from hard boards, such as glass, an acrylic board, etc. which occupied the mainstream as a transparent material, is advancing in recent years. It is mentioned that the property for which a transparent material is asked doubles with the demand of lightweight-izing of the parts not only using a mere high light transmission but a transparent material and a device, a miniaturization, low-cost-izing, the flexibility of a design, highly-efficient-izing, etc., and is developing in these electronics field as the reason. As a transparency film, the film which used methacrylic resin (PMMA), polyester (PET), the polycarbonate (PC), the polyether ether phon (PES), the polyarylate (PAR), etc. as the raw material is known well. Although a PMMA film has the outstanding optical property and surface hardness, a problem is in thermal resistance and rigidity, although a PET film makes the outstanding mechanical characteristic, thermal resistance, and chemical resistance discover, an optical anisotropy becomes large according to molecular orientation, and a birefringence is inferior in it with the extension operation under manufacture. Moreover, although PC film is a material excellent in shock resistance and thermal resistance, it is inferior to weatherability and surface hardness, and an optical property cannot be referred to as enough, either. Although it has the thermal resistance which was very excellent about PES and a PAR film, coloring is strong and there is a problem of being very expensive. Thus, since it was hard to be called that to which it is the actual condition and an advancement in recent years and the complicated demand should not necessarily be satisfied that the conventional transparency film has the advantage and demerit, respectively, an appearance of the further highly efficient nature film was desired.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the transparency film excellent in an optical property, thermal resistance, a mechanical characteristic, and surface smooth nature.

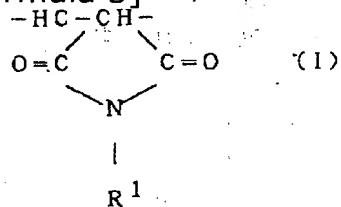
[0004]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of the above-mentioned problem, this invention persons find out that the transparency film which changes using the resin constituent which consists of a maleimide olefin system copolymer and an acrylonitrile styrene copolymer of specific composition fills the above-mentioned purpose, and came to complete this invention.

[0005] That is, the constituent (I) which shows this invention below is related with the transparency film with which it is 40 - 60-mol %, a constituent (II) is 60 - 40-mol %, and number average molecular weight is characterized by changing using the resin constituent which consists of 1 - 99 % of the weight of 1×10^3 or more maleimide olefine copolymers it is [olefine copolymers] 5×10^6 or less, and 99 - 1 % of the weight of acrylonitrile styrene copolymers which include b acrylonitrile unit 21 to 45% of the weight.

[0006]

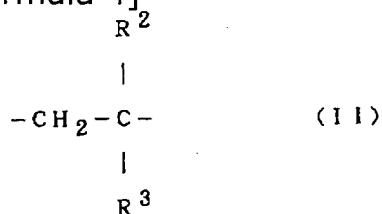
[Formula 3]



(R¹は水素または炭素数1～6のアルキル基を示す)

[0007]

[Formula 4]



(R²及びR³は各々水素または炭素数1～6のアルキル基を示す)

[0008] Hereafter, this invention is explained in detail.

[0009] The maleimide olefine copolymer which consists of an above-mentioned constituent (I) and an above-mentioned constituent (II) can be obtained by the radical copolymerization reaction of for example, maleimide and olefins. As a compound which gives a constituent (I), maleimide, such as maleimide, N-methyl maleimide, N-ethylmaleimide, N-n-propyl maleimide, N-i-propyl maleimide, N-n-butylmaleimide, N-i-butylmaleimide, N-s-butylmaleimide, N-t-butylmaleimide, N-n-pentylmaleimide, N-n-hexyl maleimide, N-cyclo propyl maleimide, N-cyclo butylmaleimide, and N-cyclohexyl maleimide, is illustrated, and N-methyl

maleimide is desirable especially from the point of thermal resistance, a mechanical characteristic, and transparency. furthermore, these compounds -- 1 a seed -- or two or more sorts can be combined and it can use

[0010] As a compound which gives a constituent (II), olefins, such as an isobutene, a 2-methyl-1-butene, 2-methyl-1-pentene, and a 2-methyl-1-hexene, can be illustrated, among these an isobutene is desirable especially from the point of thermal resistance, a mechanical characteristic, and transparency. moreover, these compounds -- one sort -- or two or more sorts can be combined and it can use The content of a constituent 1 is 40-60-mol% of the whole copolymer, and is desirable from the point of thermal resistance and a mechanical characteristic.

[45-55 mol% of] When a constituent (I) exceeds 60-mol %, since the thermal resistance of the film which becomes weak and is obtained in the case below 40 mol % falls, the film obtained is not desirable.

[0011] both a polymerization method with the well-known polymerization of these monomers, for example, a bulk-polymerization method, a solution polymerization method a suspension-polymerization method and an emulsion-polymerization method -- although -- it is employable A precipitation polymerization method is desirable especially from the transparency of the film obtained, and the point of a color tone.

[0012] As a polymerization initiator, benzoyl peroxide, lauryl peroxide, Octanoyl peroxide, acetyl peroxide, G t-butyl peroxide, Organic peroxide, such as t-butyl cumyl peroxide, dicumyl peroxide, tert-butyl peroxide acetate, and t-butyl par oxybenzoate, Or 2 and 2'-azobis (2,4-dimethylvaleronitrile), Azo system initiators, such as - azobisisobutyronitril, dimethyl-2,2'-azobisisobutyrate, and 2 and 2'-azobis (2-butyronitrile), 2, and 2 '1, 1'-azobis (cyclohexane-1-carbonitrile), are mentioned.

[0013] In a solution polymerization method, benzene, a cyclohexane, a dioxane, a tetrahydrofuran, an acetone, a methyl ethyl ketone, a dimethylformamide, isopropyl alcohol, butyl alcohol, etc. are mentioned as an usable solvent. As a solvent especially used for a precipitation polymerization; an aromatic system solvent and the mixed solvent of alcohol are desirable.

[0014] Although polymerization temperature can be suitably set up according to the decomposition temperature of an initiator, it is desirable to carry out in 40-150 degrees C generally.

[0015] An above-mentioned maleimide olefine copolymer can be obtained also by forming into back imide the resin obtained by copolymerization of a maleic anhydride and olefins using ammonia and an alkylamine.

[0016] Such a back imide-ized reaction can be manufactured by making for example, a maleic anhydride and an isobutene copolymer react at primary amine, such as alcoholic solvents, such as a melting state or a methanol, ethanol, and propanol, and the temperature of 100-350 degrees C. Here, the number average molecular weight (M_n) of the copolymer to generate can be calculated by the gel permeation chromatography (GPC). The molecular weight of a maleimide olefine copolymer has desirable or more 1×10^4 1×10^6 or less thing from the point of the balance of 1×10^3 or more 5×10^6 or less and mechanical characteristics, and a moldability. When molecular weight exceeds 5×10^6 , the front-face nature of the

film obtained becomes bad, and it is in the inclination for the film obtained to become weak at the case of 1xless than 103.

[0017] 21 - 45% of the weight of the whole composition of the acrylonitrile content of the acrylonitrile styrene copolymer used by this invention is desirable. Since it becomes opaque and thermal resistance also falls, the film obtained since the compatibility of a maleimide olefine copolymer and an acrylonitrile styrene copolymer will fall if it separates from this range is not desirable.

[0018] 10:90-90:10 from the point of the balance of 1:99-99:1 (% of the weight), processability, and thermal resistance (% of the weight) -- especially 50:50-90:10 (% of the weight) are desirable [rate / of the maleimide olefine copolymer used by this invention, and an acrylonitrile styrene copolymer] When a maleimide olefine copolymer is less than 1 % of the weight, since the thermal resistance of a film falls, it is not desirable. Moreover, since a surface dry area occurs on the film with which it becomes easy to produce the heat deterioration of an acrylonitrile copolymer, or it is acquired when a maleimide olefine copolymer exceeds 99 % of the weight, it is not desirable.

[0019] The transparency film of this invention is excellent in an optical property, and has especially the feature [hard / isotropic / slight] that a birefringence is low, optically. A birefringence is a phenomenon divided into two light waves to which the light which carried out incidence has the perpendicular oscillating direction in anisotropy material mutually, a birefringence is not produced as an optical material, that is, an optically isotropic thing is desired. Since the transparency film in this invention consists of a maleimide olefine copolymer which has a positive birefringence, and an acrylonitrile styrene copolymer which has a negative birefringence, negates each other birefringence and suits, its birefringence is small.

[0020] The transparency film of this invention is the range which does not exceed the main point of invention, in addition can add polymer, a surfactant, a polyelectrolyte, carbon black, a carbon fiber, a conductive complex, an inorganic filler, a silica, an alumina, a zeolite, a pigment, a color, a thermostabilizer, an ultraviolet ray absorbent, an antistatic agent, an anti blocking agent, lubricant, etc.

[0021] As a method of manufacturing the transparency film of this invention, the method of well-known official businesses, such as the casting method (the solution casting method), a melting extrusion method, the calender method, and compression forming, is mentioned. As solvents used for the casting method Chlorine-based solvents, such as chloroform, 1, and 2-dichloroethane, toluene, Aromatic system solvents, such as xylenes and these mixed solvents, a methanol, Alcoholic system solvents, such as ethanol, an isopropanol, n-butanol, and 2-butanol, A methyl cellosolve, ethylcellosolve, a butyl cellosolve, a dimethylformamide, A dimethyl sulfoxide, a dioxane, a tetrahydro furan, an acetone, ethyl acetate, methyl acetate, the SHIECHIRU ether, etc. can be used, and a drum formula casting machine, a band formula casting machine, a spin coater, etc. can be used as forming equipment. As a melting extrusion method, a T die method and a tubular film process are mentioned. Moreover, the tank extending method, the radiation extending method, the hot blast heating method,

the hot-platen overheating method, the roll heating method, etc. are mentioned as the tenter method, the tube method, and a uniaxial-stretching method as a NI shaft extending method which is good also as an oriented film as for the obtained film, and can adopt it by the extending method.

[0022] The thickness of the transparency film of this invention is 10-500 micrometers, and is 30-200 micrometers more preferably. When film thickness is less than 10 micrometers, a mechanical characteristic falls, and when exceeding 500 micrometers, a problem arises in flexibility.

[0023] Coating of the thin film may be carried out in order for the transparency film of this invention to give functions, such as gas barrier nature, a sex with a blemish-proof, and chemical resistance. Namely, various kinds of thermoplastics, the amino group, an imino group, an epoxy group, The thermosetting resin which has a silyl machine etc., an acryloyl machine, a methacryloyl machine, Into the mixture of the radiation-curing type resin which has a vinyl group etc., or these resins, a polymerization inhibitor, Waxes, a dispersant, a pigment, a solvent, a color, a plasticizer, an ultraviolet ray absorbent, an inorganic filler, etc. are added. The gravure roll coating method, the MAIYA bar coating method, the reverse-roll-coating method, Coating can be carried out by methods, such as the DIP coating method, the air-knife-coating method, the calender coating method, the SUKIZU coating method, the kiss coating method, the fan ten coating method, the spray coating method, and the spin coating method. Furthermore, after coating, hardening by radiation irradiation or heat curing by heating can be made to be able to perform if needed, and it can consider as a hardening thin film layer.

Moreover, in case it prints, methods, such as a gravure method, an offset method, a flexo method, and a silk screen method, can be used. Moreover, from the purpose which gives gas-seal nature etc., you may have the metallic-oxide layer which makes aluminum, silicon, magnesium, zinc, etc. a principal component, and a metallic-oxide layer is formed by the vacuum deposition method, the sputtering method, the ion plating method, and the plasma CVD method.

[0024] Moreover, it is possible to also make it laminate with other films. As a method of laminating, what method of well-known official business may be used, for example, the lamination methods, such as the thermal-bond methods, such as the heat-sealing method, the impulse-heat-sealing method, an ultrasonic-jointing method, and a RF conjugation method, the extrusion laminating method, the hot-melt laminating method, the dry-laminate method, the wet laminating method, the non-solvent-bonding laminating method, the thermal laminating method, and the co-extruding method, etc. are mentioned. As a film to laminate, a polyester resin film, a polyvinyl alcohol resin film, a cellulosic-resin film, the poly polyvinyl-fluoride film, a polyvinylidene chloride resin film, a polyacrylonitrile resin film, a Nylon film, a polyethylene-resin film, a polypropylene resin film, an acetate resin film, a polyimide resin film, a polycarbonate resin film, a polyacrylate resin film, etc. are mentioned, for example.

[0025] The following are mentioned as a use of the transparency film of this invention.

[0026] display field: -- a membrane switch and a liquid crystal display (a phase contrast film --) A polarization film, a plastics liquid crystal cell,

electroluminescence, Electrochromic one, an electrophoresis display, a plasma display panel, A field emission display, the diffusion film for back lights, Light-filter record field : An electrostatic recording substrate, OHP, a mother print, a slide film, A microfilm, X-ray film light and a magnetic memory field : Thermoplastic recording, Ferroelectric random-access memory, a magnetic tape, an ID card, a bar code antistatic field field : The aperture of meter, The Braun tube of television, a clean room aperture, semiconductor wrapping, the protection-against-dust film electromagnetic wave cover field for photo masks : A measuring instrument, Medical equipment, a radiation detector, IC parts, CRT, a liquid crystal display optoelectric-transducer field : The aperture of a solar battery, A light amplifier, a photosensor heat ray reflective field : Apertures (construction, automobile, etc.), an incandescent lamp, The aperture of cooking oven, the inspection hole of a furnace, a permselective-membrane planar-heating-element field : A defroster, The aircraft, an automobile, a freezer, an incubator, goggles, medical equipment, liquid crystal display electronic parts and a circuit material field : A capacitor, Mounting of a resistor, a thin film compound circuit, and a lead loess LSI chip carrier, a dry film resist electrode field : The electrode light-transmission filter field:ultraviolet-rays cut-off filter for paper dc-batteries, A ultraviolet filter, an ultraviolet-rays transparency visible optical-absorption filter, a color separation filter, Conversion filter for color temperature), a neutral density filter, a contrast filter, A wavelength-calibration filter, an interference filter, an infrared transparency filter, an infrared cut filter, A heat-absorbing filter, a heat ray reflective filter gas permselective-membrane field : Oxygen / nitrogen demarcation membrane, A carbon-dioxide demarcation membrane, a hydrogen demarcation membrane electric insulation field : An insulating adhesive tape, the slot liner of a motor, A interphase insulation of a transformation machine, an insulation of lead wire, the pre-insulation macromolecule sensor field of a high-voltage cable : A photosensor, An infrared sensor, an acoustic wave sensor, a pressure-sensor surface-protection field : A liquid crystal display, CRT, furniture, a built in kitchen unit, automatic in-the-car sheathing, a polarization film protection film, Paint protection film sliding material field : Lining of a hopper chute, the skid material of a band conveyor, The skid material of a guide rail, the ejection roller of a copying machine, a computer mouse porosity film field:moisture-permeation waterproofer, filter material, the other fields for micro filters: Energization hot printing, a printer ribbon, an electric wire cable shield, a leak-prevention film, the separate film for cells. [0027]

[Example] Hereafter, although an example explains this invention, this invention is not limited to an example.

[0028] The molecular weight of generation polymer was calculated by polystyrene conversion using the gel permeation chromatography (GPC, HLC[by TOSOH CORP.]-802A). Elemental analysis and 1 H-NMR measurement mainly determined composition of generation polymer. The glass transition temperature of the obtained polymer was measured by part for 10 degrees-C/of programming rates using DSC (by SEIKO electronic industry incorporated company DSC200). All light transmissions are ASTM. It measured according to D1003 (1996). The birefringence was measured using the ellipsometer. Young's modulus is ASTM about

ASTM and **** breaking strength. It measured according to D882 (1996). Surface roughness (smooth nature) was measured according to JISB0601 (1996).

[0029] After teaching 15l. (1:1-fold quantitative ratio) of mixed solvents of N-methyl maleimide 1.2kg, 8g of t-butylperoxy neodecanoate, toluene, and a methanol to 30l. autoclave to which the synthetic agitator of a synthetic example maleimide olefine copolymer, the nitrogen introduction pipe, the thermometer and the deaeration pipe, and the thermometer were attached and purging several times with nitrogen, isobutene 8.5l. was taught and the reaction was performed at 60 degrees C for 6 hours. The obtained particle was dried after centrifugal separation. Yield was 1.7kg.

[0030] From the elemental-analysis result (C; 64.7 % of the weight, H; 7.8 % of the weight, N; 8.4 % of the weight) of the obtained polymer, the maleimide unit and isobutene unit in generation polymer were 50-mol %, respectively. The obtained polymer was number average molecular weight (Mn) 95000.

[0031] The acrylonitrile styrene copolymer from which the acrylonitrile content of a publication differs in N-methyl maleimide isobutene copolymer and Table 1 which were compounded in the example 1, the example 2 and the example 1 of comparison - the example of example of comparison 5 reference was shaked equivalent [every], respectively, and with the 30mmphi biaxial extruder (Japan Steel Works Make), melting kneading extrusion was performed and it considered as the pellet. And the pellet obtained by the T-die extruder made to connect T-dice to a lab plastic strike mill biaxial extruder (Oriental energy machine incorporated company make) was supplied and fabricated, and the film with a thickness of 100 micrometers was obtained. The physical-properties measurement result of the obtained film was shown in Table 1. While the acrylonitrile content of an acrylonitrile styrene copolymer is 21-45-mol %, the film obtained shows a single glass transition temperature, and is excellent in transparency. This shows that both are compatibility in this range. On the other hand, when an acrylonitrile content exceeded less than [21 mol %] and 45-mol %, the film obtained has two glass transition temperatures, and the film obtained became cloudy. In this range, it turns out that both are non-compatibility. Although both were non-compatibility and the example 5 of comparison had high transparency, the thermal resistance of the film with which this is a phenomenon on the appearance for becoming closely, and both refractive index is obtained became low.

[0032]

[Table 1]

	アクリニトリル含量 (重量%)	ガラス転移温度 (℃)	光線透過率 (%)
実施例1	25	117	93
実施例2	30	121	93
比較例1	6	103,155	60
比較例2	11	102,151	65
比較例3	20	105,151	68
比較例4	46	107,147	75
比較例5	57	109,150	88

[0033] After carrying out melting kneading like the method of an example 1 and an example 2 and pelletizing N-methyl maleimide isobutene copolymer

compounded in the example 3 - the example 5 and the example 6 of comparison, and the example of example of comparison 7 reference, and an acrylonitrile styrene copolymer (acrylonitrile content % of 30 mols) by the composition ratio shown in Table 2, membranes were formed on the film with a thickness of 100 micrometers. The physical-properties measurement result of the obtained film was shown in Table 2.

[0034]

[Table 2]

	実施例3	実施例4	実施例5	比較例6	比較例7
メタレド・イブン共重合体/アクリロトリル-メソ共重合体(重量比)	75 /25	50 /50	25 /75	100 /0	0 /100
ガラス転移温度 (°C)	135	117	122	155	98
光線透過率 (%)	93	92	91	93	92
複屈折 (nm)	4	5	7	40	12
ヤング率 (Mpa)	3800	3600	3400	4800	3300
引張破壊強度(MPa)	810	770	720	880	650
表面粗さ Ra(nm)	15	18	19	40	20

Birefringence
Young's modulus
UTS
Surface Roughness

[0035]

[Effect of the Invention] It excels in thermal resistance, the transparency film of this invention has good transparency and a small birefringence, and since it has the outstanding mechanical characteristic, it can use them for the use asked for advanced and complicated properties including an electronics field, so that more clearly than an example.

[0036]

[Translation done.]